Spatial Distribution of Perfluorinated Organic Compounds in Surface Marine Sediments from the Seto Inland Sea, Japan

Asaoka, Satoshi ; Yoshiki, Ryosuke ; Haga, Yuki ; Matsumura, Chisato ; Umehara, Akira ; Takeda, Kazuhiko

(Citation)
Journal of Water and Environment Technology,18(4):226-237

(Issue Date)
2020

(Resource Type)
journal article

(Version)
Version of Record

(URL)
https://hdl.handle.net/20.500.14094/90007354

doi: 10.2965/jwet.19-146 Journal of Water and Environment Technology, Vol.18, No.4: 226–237, 2020

Original Article

Spatial Distribution of Perfluorinated Organic Compounds in Surface Marine Sediments from the Seto Inland Sea, Japan

Satoshi Asaoka [a], Ryosuke Yoshiki [b], Yuki Haga [b], Chisato Matsumura [b], Akira Umehara [c], Kazuhiko Takeda [d]

[a] *Research Center for Inland Seas, Kobe University, Kobe, Japan*
[b] *Hyogo Prefectural Institute of Environmental Sciences, Kobe, Japan*
[c] *Environmental Research and Management Center, Hiroshima University, Higashihiroshima, Japan*
[d] *Graduate School of Integrated Science of Life, Hiroshima University, Higashihiroshima, Japan*

ABSTRACT

Perfluoroalkyl substances (PFASs) such as perfluorocarboxylic acid (PFCAs) and perfluoroalkane sulfonates (PFSAs) are persistent, bioaccumulative, and toxic substances that are distributed worldwide. Here we investigated the current concentrations of PFASs in the surface sediments from the Seto Inland Sea, Japan. The concentrations of PFCAs in surface sediments from the Sea ranged from 0.05 to 0.67 ng g^{-1}. Perfluoroundecanoic acid (PFUnDA) was detected at all 15 sampling stations; its concentration was 0.05–0.24 ng g^{-1}. Perfluorohexanoic acid (PFHxA), which is used as an alternative to perfluorooctanoic acid (PFOA), was detected in Osaka Bay and Kii Channel. The contamination of PFCAs in the sediment from Osaka Bay and Kii Channel is shifting to PFHxA. In contrast, only perfluorooctanesulfonic acid (PFOS) was detected at the center part of the bays in the Sea. The significant positive correlation between the PFCAs concentrations in the sediment and the sedimentation rates was observed in the Sea. Hence, the concentration of PFCAs in surface sediments from the Sea was controlled by the sedimentation rate.

Keywords: perfluoroalkyl substance, perfluorocarboxylic acid, perfluorohexanoic acid, perfluoroundecanoic acid, persistent organic pollutant

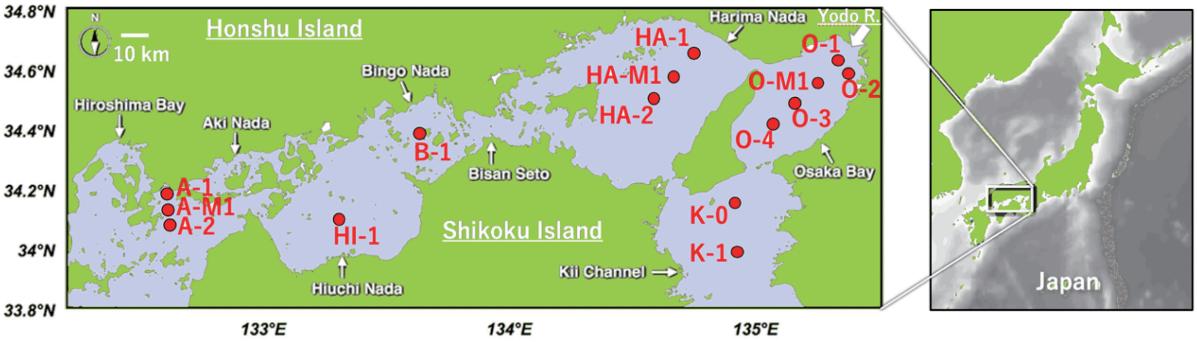
INTRODUCTION

Perfluoroalkyl substances (PFASs) such as perfluorocarboxylic acid (PFCAs) and perfluoroalkane sulfonates (PFSAs) are widely used as non-stick cookware, waterproofing treatments in outdoor clothing, fabric, furniture and carpet, waterproof coatings for paper and cardboard, mist suppressants in the metal plating industry and fire-fighting foams [1]. PFASs have been detected worldwide in surface water, groundwater, seawater, drinking water, and organisms [2–5], as PFASs are stable and persistent in the environment [6,7]. Due to their bioaccumulation through the food chain, PFASs have a negative impact on top predator species [8–10].

In 2009, perfluorooctanesulfonic acid (PFOS) was added to the Stockholm Convention listing of persistent organic pollutants, and the uses of PFOS are currently strictly controlled. Perfluorooctanoic acid (PFOA) and other PFCAs are also regulated in the EU and Canada [11]. Along with these regulations, shorter-chain PFASs such as perfluorobutane sulfonic acid (PFBS) or perfluorohexanoic acid (PFHxS) are currently being developed as alternatives to long-chain PFASs [11]. The continuous monitoring and assessment of PFASs thus remains necessary.

The Seto Inland Sea is the largest semi-enclosed sea in Japan, with both a eutrophic area (facing one of the most industrialized and populated areas affected by terrigeneous loads) and an oligotrophic and less populated area. Monitoring of PFASs in coastal sea water and river water

Corresponding author: Satoshi Asaoka, E-mail: s-asaoka@maritime.kobe-u.ac.jp
Received: November 3, 2019, Accepted: May 5, 2020, Published online: August 10, 2020



Map of sampling stations were drawn using software for the analysis and visualization of oceanographic and meteorological data sets, Ocean Data View ver. 4.7.10.

Fig. 1 Sampling stations in the Seto Inland Sea, Japan.

in the Seto Inland Sea has been conducted [12–14], but few recent investigations of PFASs in sediments from this Sea have been reported. Sediments that have settled in enclosed water bodies are affected by significant terrigenous loads. Chemical pollution is thus closely associated with domestic and industrial activities in coastal areas.

The purposes of this study are to (1) determine the current concentrations of PFASs in sediments from the Seto Inland Sea, and (2) identify the factor(s) that may affect the PFASs concentrations of those surface sediments.

MATERIALS AND METHODS

Sediment and marine particulate matter sampling sites

Sediment and marine particulate matter samples were collected from 15 stations in the Seto Inland Sea, Japan on 4th-8th July or 14th-17th November in 2016 and 3th-7th July in 2017 by a Hiroshima University training and research vessel, the Toyoshio Maru (**Fig. 1**). The coordinates of the sampling sites are shown in Supplemental **Table S1**. The Seto Inland Sea is a semi-enclosed sea approx. 450 km from east to west and 15–55 km from north to south, with an average depth of 38 m. The sea is surrounded by three of Japanese five main islands (Honshu Island, Shikoku Island, and Kyushu Island) and contains more than 700 islands. The total area of the sea is 23,203 km^2, and the catchment is one of the most industrialized and populated areas in Japan, with a watershed population of approx. 30 million.

Sampling procedures

The sediment core sampling was carried out using an undisturbed core sampler (11 cm dia., 50 cm long: HR type; Rigo, Osaka, Japan) on the training and research vessel. The collected cores were cut at 5-cm intervals on board the vessel. Each collected sediment sample was immediately transferred into a methanol-rinsed stainless steel container and stored in a refrigerator at 4°C before being transferred to the laboratory.

Sample extraction for the analysis of PFASs

Each weighed sediment sample (approx. 10 g-wet) was taken to a 50-mL glass tube; then, 40 µL of 100 µg L^{-1} MPFAC-MXA containing perfluoro-n-[$^{13}C_4$]butanoic acid (MPFBA), perfluoro-n-[1,2-$^{13}C_2$]hexanoic acid (MPFHxA), perfluoro-n-[1,2,3,4-$^{13}C_4$]octanoic acid (MPFOA), perfluoro-n-[1,2,3,4,5-$^{13}C_5$]nonanoic acid (MPFNA), perfluoro-n-[1,2-$^{13}C_2$] decanoic acid (MPFDA), perfluoro-n-[1,2-$^{13}C_2$] undecanoic acid (MPFUnDA), perfluoro-n-[1,2-$^{13}C_2$]dodecanoic acid (MPFDoDA), sodium perfluoro-1-hexane[$^{18}O_2$] sulfonate (MPFHxS), and sodium perfluoro-1-[1,2,3,4-$^{13}C_4$] octanesulfonate (MPFOS) was purchased from Wellington Laboratories, Inc., Ontario, Canada as a surrogate and 20 mL of methanol (LC/MS grade; FujiFilm Wako Pure Chemicals, Osaka, Japan) were mixed together and the mixture was ultrasonicated for 15 min. After centrifugation at 3000 rpm for 10 min, the methanol phase was transferred to a 200-mL glass concentration tube. The PFASs in the residuals were extracted by adding 20 mL of the methanol to the residuals twice.

The extracts were combined together and concentrated to approx. 5 mL by purging a gentle high-purity N_2 gas stream with the use of a pressured gas blowing concentrator (Turbo Vap II; Biotage, Uppsala, Sweden). The concentrated extract was filtered through a glass-fiber filter (GF/B; Whatman, Maidstone, UK) and the filtrate was transferred to a 200-mL glass beaker. Next, 100 mL of ultrapure water and 10 µL of 98% formic acid (special grade; FujiFilm Wako Pure

Chemicals) were added to the filtrate. Thereafter the filtrate was cleaned up by solid phase extraction using a sample pretreatment column (Presep PFC-II; FujiFilm Wako Pure Chemicals). The glass beaker was rinsed with 5 mL of ultrapure water, and the rinsed solution was also introduced to the Presep PFC-II column.

Successively, the retained PFASs were eluted by introducing 5 mL of a 0.1% ammonia/methanol solution to the Presep PFC-II column. The eluted PFASs solution was concentrated to approx. 1 mL by purging a gentle high purity N_2 gas stream using the Turbo Vap LV pressured gas blowing concentrator. Finally, 10 µL of 100 µg L^{-1} $^{13}C_8$ - perfluorooctanoic acid ($^{13}C_8$ PFOA) (Wellington Laboratories) as a syringe spike was added to the concentrated solution to determine concentrations of PFASs.

Sample analyses

We analyzed the concentrations of PFASs in the extracts based on the report by Takemine *et al.* (2014) [13]. PFCAs and PFASs were determined by LC-MS/MS using a Xevo tandem quadrupole (TQ) MS (Waters, Milford, USA) coupled with an Acquity UPLC (Waters).We used 2 mol L^{-1} of ammonium acetate (HPLC grade; FujiFilm Wako Pure Chemicals) and acetonitrile (LC/MS grade; Kanto Kagaku, Tokyo, Japan) as an eluent; they were delivered at a flow rate of 0.3 mL min^{-1}. The gradient of the acetonitrile concentration was programmed as follows: 1% to 95% at 0–8 min, 95% at 8–9 min, and 95% to 1% at 9.0–9.1 min. Total time for analysis was 10 min. The extract (5 µL) was injected onto a C18 column (ACQUITY UPLC BEH, 2.1×50 mm; Waters). The column temperature was set at 40°C. The tandem mass spectrometer was operated in the electrospray ionization mode (ESI-negative). The source temperature was set at 150°C with 0.5 kV as the capillary voltage and 600°C as the desolvation temperature. The flow rates were as follows: desolvation gas (N_2 gas), 1000 L h^{-1}; cone gas (N_2 gas), 50 L h^{-1}, and collision gas (Ar gas) 0.15 mL min^{-1}.

The instrumental limits of detection (LOD) were defined empirically as the concentration producing a signal to noise ratio of 3, and the limits of quantification (LOQ) were defined as the concentration producing a signal to noise ratio of 10. The method limits of detection (MDL) and method limits of quantification (MQL) were determined from LODs and LOQs as described previously [15]. MDLs of PFCAs and PFSAs were 0.01 ng g^{-1} and 0.02 ng g^{-1} respectively. MQLs of PFCAs and PFSAs were 0.03 ng g^{-1} and 0.06 ng g^{-1} respectively.

Target compounds were quantified using the isotope dilution method for the corresponding MPFAC-MXA according to a formula described previously [13]. The average surrogate recoveries for all samples were as follows: perfluorobutanoic acid (MPFBA) (71.4%), MPFHxA (74.9%), MPFOA (71.0%), perfluorononanoic acid (MPFNA) (79.1%), perfluorodecanoic acid (MPFDA) (72.9%), MPFUnDA (71.0%), perfluorododecanoic acid (MPFDoDA) (66.5%), perfluorohexane sulfonate (MPFHxS) (95.6%), and MPFOS (102%).

RESULTS AND DISCUSSION

The concentrations of PFCAs in the sediment samples

The concentrations of PFCAs in the surface sediments from the Seto Inland Sea ranged from 0.05 to 0.67 ng g^{-1} (**Table 1 and Fig. S1**). Higher concentrations of PFCAs were observed at stations HA-2 (0.63 ng g^{-1}) and O-4 (0.67 ng g^{-1}) compared to the other stations (0.05–0.49 ng g^{-1}). The PFTeDA was not quantified except for stations O-1 (0.08 ng g^{-1}) and O-2 (0.06 ng g^{-1}). The concentrations of PFPeA and PFOcDA were below the limit of detection (< 0.01 ng g^{-1}) or the limits of quantification (< 0.03 ng g^{-1}) at all sampling stations. In contrast, PFUnDA was detected at all sampling stations, and its concentration ranged from 0.05 to 0.24 ng g^{-1}. Compared to the recently obtained concentrations of PFCAs in sediments from different areas around the world (**Table 2**), the concentrations of PFCAs in surface sediments from the Seto Inland Sea collected in this study were the same or lower compared to those from different areas around the world.

The percent compositions of PFCAs in the surface sediments from the Seto Inland Sea are illustrated in **Fig. 2**. The PFNA was a relatively high component at 29.1%–47.5% of the total PFCAs at the western sampling stations (Stns. A-1 to HI-1) compared to the other stations; i.e., PFNA was a minor component at 0%–16.5% of the total PFCAs at the middle and eastern sampling stations (Stns. B-1 to K-1). PFHxA was characteristically detected at the inner part of Osaka Bay (Stns. O-1, O-M1 and O-2) and the Kii Channel (Stns. K-0 and K-1). PFHxA is currently used as an alternative to PFOA, and our PFHxA results demonstrate the contamination by alternatives to PFOA in the surface sediments collected from Osaka Bay and Kii Channel.

The numbers of PFCAs detected in the sediments differed among the sampling stations. At Osaka Bay (Stns. O-1 to O-4) and Kii Channel (Stns. K-0 and K-1), 10 species of PFCAs were detected, whereas at the other sampling stations, five species of PFCAs at most were detected. The difference in the

Table 1 The concentrations of PFCAs in surface sediments (0–5 cm layer) from the Seto Inland Sea, Japan (ng g^{-1} d. w.).

Stn.	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFHxDA	PFOcDA	PFCAs
A-1	< MDL	< MDL	< MDL	< MDL	0.10	0.06	< 0.03	0.06	< MDL	< 0.03	< MDL	< MDL	< MDL	0.22
A-M1	< MDL	< MDL	< MDL	< MDL	< 0.03	0.10	0.07	0.10	< MDL	0.06	< MDL	< MDL	< MDL	0.32
A-2	< MDL	< MDL	< 0.03	< MDL	< 0.03	0.10	< 0.03	0.11	< MDL	< 0.03	< 0.03	< MDL	< MDL	0.21
HI-1	< MDL	< MDL	< 0.03	< 0.03	0.10	0.14	< 0.03	0.10	< MDL	0.06	< 0.03	< MDL	< MDL	0.40
B-1	< MDL	< MDL	< MDL	< MDL	< 0.03	< 0.03	< 0.03	0.05	< 0.03	< 0.03	< 0.03	< MDL	< MDL	0.05
HA-1	< MDL	< MDL	< MDL	< MDL	< 0.03	< 0.03	< 0.03	0.08	< 0.03	0.05	< 0.03	< MDL	< MDL	0.12
HA-M1	< MDL	< MDL	< 0.03	< MDL	< 0.03	< 0.03	0.10	0.11	< 0.03	< 0.03	< 0.03	< MDL	< MDL	0.21
HA-2	< MDL	< MDL	< 0.03	< MDL	0.18	0.10	0.11	0.24	< 0.03	< 0.03	< 0.03	< MDL	< MDL	0.63
O-1	< MDL	< MDL	0.09	< MDL	< 0.03	< 0.03	< 0.03	0.07	< 0.03	0.10	0.08	< MDL	< MDL	0.34
O-M1	< MDL	< MDL	0.07	< MDL	< 0.03	< 0.03	0.08	0.18	< 0.03	0.10	< 0.03	< MDL	< MDL	0.43
O-2	< 0.03	< 0.03	0.17	0.07	0.05	< MDL	< 0.03	0.06	0.06	0.04	0.06	< 0.03	< MDL	0.49
O-3	< MDL	< MDL	< 0.03	< MDL	< 0.03	< 0.03	< 0.03	0.11	< 0.03	0.06	< 0.03	< MDL	< MDL	0.17
O-4	< MDL	< MDL	< 0.03	< MDL	0.09	0.12	0.13	0.20	0.06	0.07	< 0.03	< MDL	< MDL	0.67
K-0	0.04	< 0.03	0.10	< 0.03	0.09	0.05	0.06	0.08	0.03	0.04	< 0.03	< 0.03	< MDL	0.49
K-1	< MDL	< 0.03	0.09	0.03	0.04	< MDL	0.04	0.05	< 0.03	0.03	< 0.03	< 0.03	< MDL	0.28

MDL: Method detection limit (< 0.01 ng g^{-1}).

Table 2 The concentrations of PFCAs in the sediments from different areas around the world (ng g^{-1} d. w.).

Location	Year	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA
Seto Inland Sea, Japan	2016, 2017	< 0.01–0.04	< 0.03	< 0.01–0.17	< 0.01–0.07	< 0.03–0.18	< 0.01–0.14	< 0.03–0.13
Lake Hazen, Canada	2011	–	–	< 0.002	0.009	0.05	0.059	< 0.001
Yellow River, China	2013	0.050–0.344	0.230–2.18	0.013–0.190	0.041–0.744	3.23–7.80	0.963–2.83	1.33–2.39
Elbe Estuary, Germany	2016, 2017	< 0.029–0.30	–	< 0.037–0.044	< 0.011–0.018	< 0.067–0.084	< 0.0015–0.051	0.0077–0.21
Baltic Sea, Germany	2016, 2017	0.13–0.22	–	< 0.037	< 0.011–0.050	0.067–0.39	0.034–0.28	0.021–0.20
Dong Nai River etc., Vietnam	2013-2015	–	–	< 0.16	< 0.23	< 0.20	< 0.10	< 0.06–0.17
Jucar Basin, Spain	2010	5.85	0.93	MDL	0.14	1.32	0.24	0.23
Bering Sea, Chukchi Sea	2010	0.02–0.68	0.02–0.10	0.02–0.19	0.01–0.08	0.08–0.74	0.01–0.17	0.01–0.04

Location	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFHxDA	PFOcDA	Reference
Seto Inland Sea, Japan	0.05–0.24	< 0.01–0.06	< 0.03–0.10	< 0.01–0.08	< 0.03	< 0.01	This study
Lake Hazen, Canada	< 0.001	< 0.001	< 0.001	–	–	–	[16]
Yellow River, China	0.903–2.06	0.593–1.57	–	–	–	–	[17]
Elbe Estuary, Germany	0.0076–0.17	0.0059–0.14	0.0058–0.068	< 0.0032–0.036	–	–	[4]
Baltic Sea, Germany	0.030–0.27	0.0083–0.063	0.014–0.10	< 0.0032–0.022	–	–	[4]
Dong Nai River, Vietnam	< 0.06–0.24	< 0.05–0.16	< 0.03–0.16	< 0.13	–	–	[18]
Jucar Basin, Spain	MDL	MDL	MDL	0.46	MDL	MDL	[19]
Bering Sea, Chukchi Sea	0.02–0.06	0.01–0.50	0.03–0.39	–	–	–	[20]

MDL: Method detection limit.

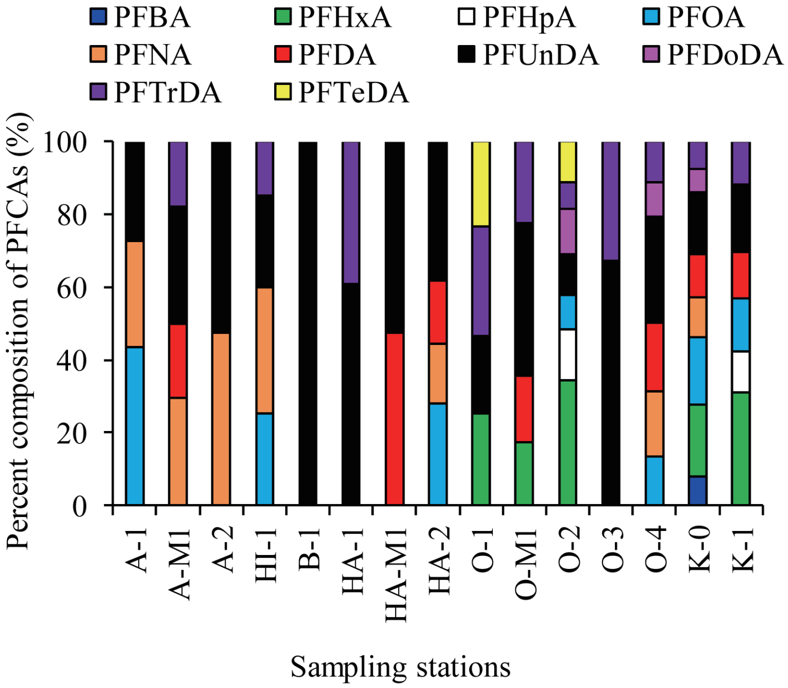


Fig. 2 Percent composition of PFCAs in surface sediments from the Seto Inland Sea.

number of PFCA species detected in the surface sediments might be attributable to the difference in the composition of PFCAs in the terrigeneous load. For example, Osaka Bay is significantly affected by the terrigeneous load from the Yodo River (catchment area: 8,240 km^2, yearly average discharge: 267.51 m^3 s^{-1}). The dominant component of PFCAs in the Yodo River and its major branch flows were PFOA, PFHpA, PFNA, PFDA, and PFUnDA [21]. Thus, the detection of many PFCA species in the Yodo River implies their use and formation in the Yodo River catchment. Kii Channel is affected by the intrusion of sea water derived from Osaka Bay. The long-chain PFASs were adsorbed suspended particulate matter (SPM) in river and transported to ocean [17]. We thus speculate that the large number of PFCAs species discharged from the Yodo River to Osaka Bay flow out to Kii Channel and were thus detected in the surface sediment at Osaka Bay (Stns. O-1 to O-4) and Kii Channel (Stns. K-0 and K-1).

In contrast, the northern part of Harimanada is affected by the terrigeneous load from the Kako River (catchment area: 1730 km^2, yearly average discharge: 45.89 m^3 s^{-1}). The dominant components of PFCAs in the Kako River were only PFOA and PFBA [13], indicating that the number of PFCA species discharged from the Kako River to the northern part of Harimanada was much smaller than the number of PFCA species in Osaka Bay discharged from the Yodo River. We therefore hypothesize that the number of PFCA species detected in the surface sediments from Harimanada was much lower than those of Osaka Bay and Kii Channel. However, the composition of PFCAs in these river waters and in these sediments were not in good agreement with each other. This might be due to the difference in the partitioning coefficients of each PFCA between sediment and the dissolved phase [4,22]. For example, in the cause of PFCAs, an increase of the organic carbon normalized partition coefficient between sediment and water (log K_{OC}) with increasing number of perfluoroalkyl moieties could be observed from PFHpA to PFUnDA [4,22].

We analyzed the vertical profile of the PFCAs in the surface sediment samples collected from Stn. O-1 because we were able to collect an undisturbed core sample at that station (**Fig. 3**). Sediment core dating was conducted using the ^{137}Cs and ^{210}Pb dating techniques. Based on the excess activity of the isotope Pb^{210}, the sedimentation rate was 0.956 cm y^{-1} for the year of 1968–2015 and the surface layer at the depth 0–10 cm was slightly affected by bioturbation, and we thus interpret the PFCAs detected in the 0–10-cm layer as the average concentration of PFCAs from 2005 to 2015. The total concentration of PFCAs at Stn. O-1 was peak at 1995 to

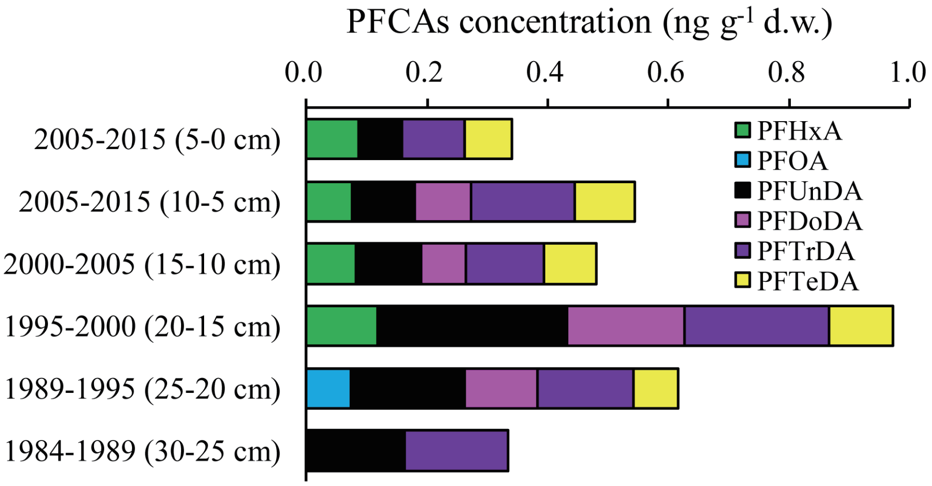


Fig. 3 Vertical profile of PFCAs concentrations in sediment collected from Stn. O-1.

2000 (0.97 ng g^{-1}). The year of the PFCAs' peak was substantially consistent with that of Tokyo Bay (2001 to 2002), Japan [23]. PFTeDA was detected after 1989. PFOA was detected in 1989–1995, whereas PFOA was below the quantification limits (< 0.06 ng g^{-1}) after 1995. In contrast, PFHxA was newly detected in after 1995; it was below the quantification limit (< 0.03 ng g^{-1}) before 1995. These data reflect the changes in the manufacturing process of fluororesins. More recently, some manufacturers have used PFHxA used as an alternative to PFOA because PFHxA is less toxic than PFOA [24]. However, the year of PFHxA detection in the sediment core sample was approximately 10 years earlier than the year of the changes in manufacturing process of fluororesins. It is possible that horizontal sediment pore water migration for short chain PFCAs can change the vertical contamination profile of sediment core samples [23]. It is considered that PFHxA in sediment pore water of the surface layer migrated to the deeper layers.

A positive correlation was reported between the concentrations of some per- and polyfluoroalkyl compounds and the organic matter concentration in sediment from Tokyo Bay. Organic matter may have an influence on the distribution of PFASs in the sediments of Tokyo Bay [23]. In contrast to Tokyo Bay, we did not detect a positive correlation between the PFCA concentrations and the orgasmic matter concentration in the sediment from the Seto Inland Sea ($r = 0.496$, $p < 0.06$). However, we observed a significant positive correlation between the PFCA concentrations in the sediment samples and the sedimentation rates [25–29] near the sampling stations ($r = 0.935$, $p < 0.00003$; **Fig. 4**) except for Kii Channel (Stns. K-0 and K-1; because no sedimentation rate data were available, we could not evaluate the relationship at K-0 and K-1). As shown in **Fig. 4**, the PFCAs concentrations in the surface sediments at the sampling sites (except for those in Kii Channel) were controlled by the sedimentation rate. The organic matter in the surface sediments originated from marine particulate organic matter (POM) because the carbon and nitrogen isotopes corresponding to the $\delta^{13}C$ and $\delta^{15}N$ values of the sediment collected from the Seto Inland Sea ranged from −21.41 to −20.31 and from 5.28 to 8.79, respectively [25]. The PFASs with a high partitioning coefficient could interact with SPM at the particle/water interface, leading to the removal of the PFASs from the water column and their accumulation in sediment [22]. We therefore speculate that the sedimentation of marine POM-adsorbed PFCAs is one of the driving forces in the accumulation of PFCAs in sediment of the Seto Inland Sea. We thus roughly estimated the sedimentation flux from the sedimentation rate [26–29] and the concentration of PFCAs in the sediments (**Fig. 5**). We observed a relatively high sedimentation flux of PFCAs (110–270 pg cm^{-2} y^{-1}) at the center of Osaka Bay (Stns.HI-1, HA-2, O-M1, O-2 and O-4).

The concentrations of PFSAs in the sediment samples

The concentrations of PFBS, PFHxS, and PFDS in the sediments were below the limit of detection (< 0.02 ng g^{-1}) at all sampling stations (**Table 3**). In contrast, PFOS was quantified at the center part of Osaka Bay; that is, the PFOS concentrations were high at Stations HI-1 (0.12 ng g^{-1}), HA-M1 (0.13 ng g^{-1}), HA-2 (0.15 ng g^{-1}), and O-M1 (0.16 ng g^{-1}) compared to those at the other 11 stations (below the limit

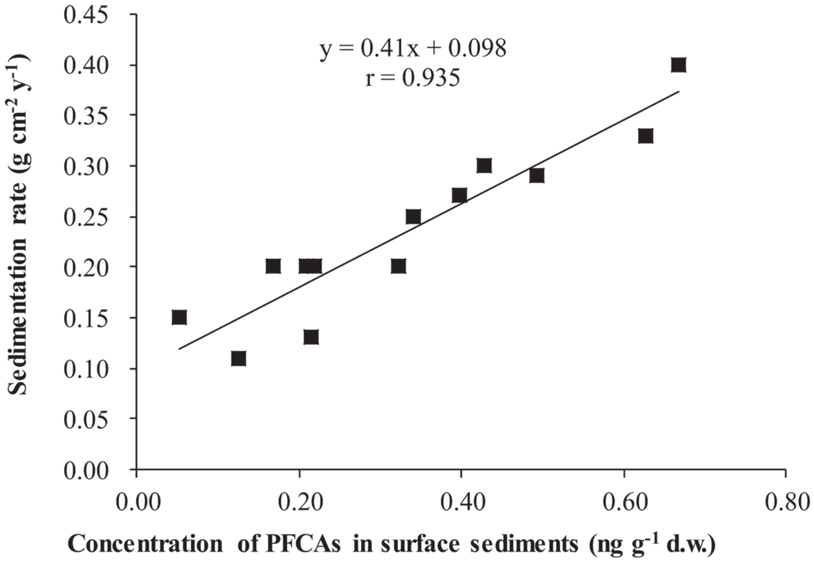


Fig. 4 The relationship between the sedimentation rate and the concentrations of PFCAs in surface sediments from the Seto Inland Sea.

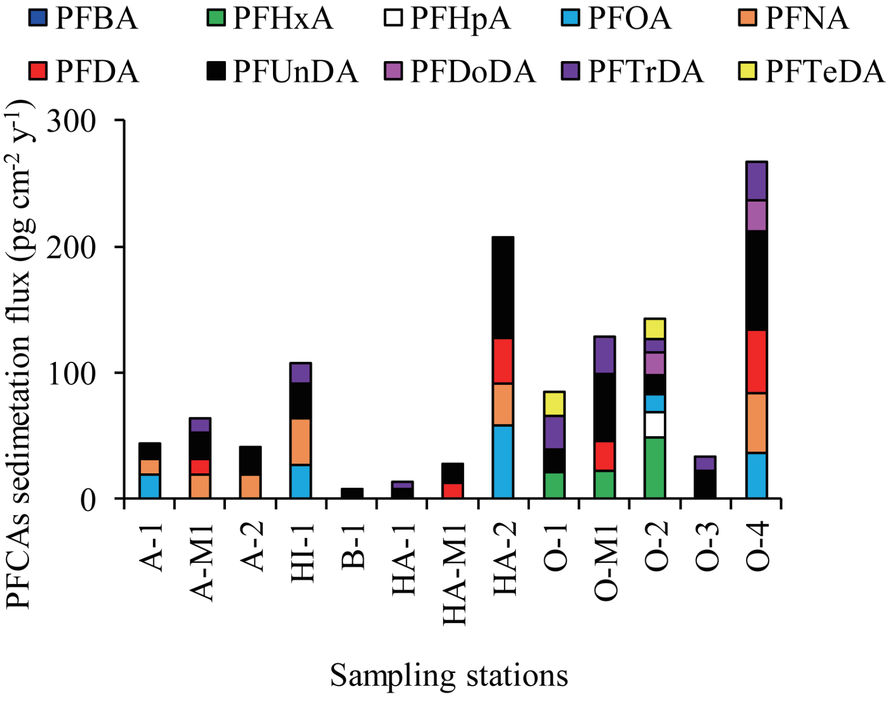


Fig. 5 The sedimentation flux of PFCAs in the Seto Inland Sea.

of quantification: < 0.06 ng g^{-1}; **Table 3**). Compared to the concentrations of PFSAs in the sediments from different areas worldwide (**Table 4**), the surface sediments from the Seto Inland Sea were at an equal or lower pollution level. The rough estimates of sedimentation flux of PFOS were as follows: 33 pg cm^{-2} y^{-1} at Stn. HI-1, 18 pg cm^{-2} y^{-1} at Stn. HA-M1, 51 pg cm^{-2} y^{-1} at Stn. HA-2, and 48 pg cm^{-2} y^{-1} at Stn. O-M1.

The vertical profiles of PFOS are summarized in **Fig. 6**. PFOS was detected in 1984–2005, but the PFOS was below the quantification limit (< 0.06 ng g^{-1}) in 2005–2015, which is consistent with the eventual regulation of PFOS under the

Table 3 Concentrations of PFSAs in the surface sediment (0–5-cm layer) from the Seto Inland Sea, Japan (ng g^{-1} d.w.).

Stn.	PFBS	PFHxS	PFOS	PFDS
A-1	< MDL	< MDL	< 0.06	< MDL
A-M1	< MDL	< MDL	< 0.06	< MDL
A-2	< MDL	< MDL	< 0.06	< MDL
HI-1	< MDL	< MDL	0.12	< MDL
B-1	< MDL	< MDL	< 0.06	< MDL
HA-1	< MDL	< MDL	< 0.06	< MDL
HA-M1	< MDL	< MDL	0.13	< MDL
HA-2	< MDL	< MDL	0.15	< MDL
O-1	< MDL	< MDL	< 0.06	< MDL
O-M1	< MDL	< MDL	0.16	< MDL
O-2	< MDL	< MDL	< 0.06	< MDL
O-3	< MDL	< MDL	< 0.06	< MDL
O-4	< MDL	< MDL	< 0.06	< MDL
K-0	< MDL	< MDL	< 0.06	< MDL
K-1	< MDL	< MDL	< 0.06	< MDL

MDL: Method detection limit (< 0.02 ng g^{-1}).

Table 4 Concentrations of PFSAs in sediments from different areas worldwide (ng g^{-1} d. w.).

Location	Year	PFBS	PFHxS	PFOS	PFDS	Reference
Seto Inland Sea, Japan	2016, 2017	< 0.02	< 0.02	< 0.06-0.16	< 0.02	This study
Lake Hazen, Canada	2011	0.022	< 0.003	0.016	–	[16]
Yellow River, China	2013	MDL–0.441	–	0.192–0.710	–	[17]
Elbe Estuary, Germany	2016, 2017	–	< 0.036–0.16	< 0.012–0.37	–	[4]
Baltic Sea, Germany	2016, 2017	–	< 0.036	0.074–0.38	–	[4]
Dong Nai River etc., Vietnam	2013–2015	< 0.34–0.57	< 0.04–18.3	< 0.08–6.72	< 0.30–0.85	[18]
Jucar Basin, Spain	2010	2.17–29.2	MDL	0.06–9.83	MDL	[19]
Bering Sea, Chukchi Sea	2010	0.01–0.60	0.02–0.15	0.03–0.20	0.01–0.09	[20]

Stockholm Convention on Persistent Organic Pollutants. After 2009, the production, use, import, and export of PFOS were strictly controlled under the Stockholm Convention.

CONCLUSIONS

The results of our investigation demonstrate that the concentration of PFCAs in surface sediments from the Seto Inland Sea, Japan was controlled by the sedimentation rate. The concentrations of PFCAs in the surface of sediments from the Sea ranged from 0.05 to 0.67 ng g^{-1}. PFUnDA was detected at all 15 sampling stations, and its concentration ranged from 0.05 to 0.24 ng g^{-1}. PFHxA which is used as an alternative to PFOS and PFOA was also observed in Osaka Bay and Kii Channel. Hence, the PFASs contamination in the surface sediment from Osaka Bay and Kii Channel is shifting to alternatives to PFOA. In contrast, PFOS was detected only at the center part of bays in the Sea. Continuous monitoring and assessments of alternatives to PFOA remain necessary to reveal the historical change of emission of alternatives.

ACKNOWLEDGEMENTS

This study was supported in part by the Japan Society for the Promotion of Science (JSPS KAKENHI) with a Grant-in-Aid for Young Scientists A, grant no. 16H05892, and the Environmental Research and Technology Development Fund (5-1602) of the Ministry of the Environment, Japan. We thank the captain and crew members of the Toyoshio Maru for their help with the sampling. We also thank Dr. Hideo Yamazaki, Kinki University for his help with the sediment core dating.

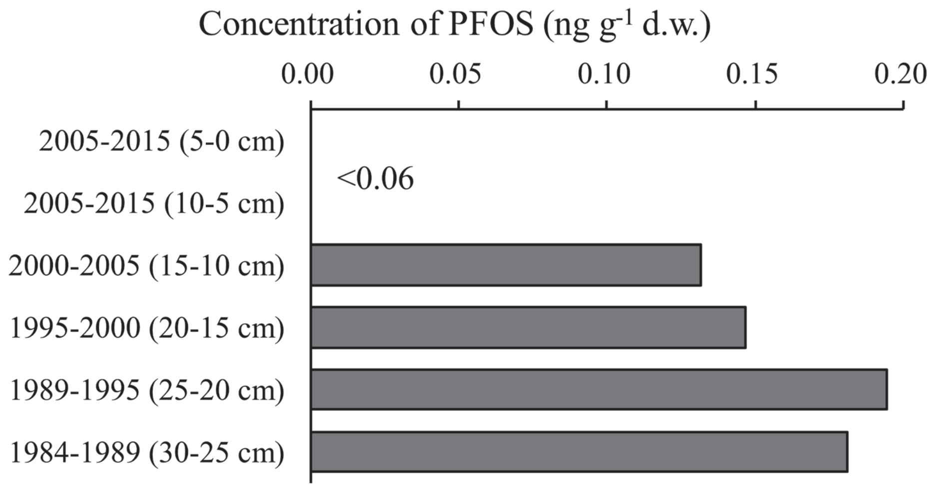


Fig. 6 Vertical profile of PFOS concentrations in sediment collected from Stn. O-1.

SUPPLEMENTARY MATERIALS

Supplementary Materials file for this article is available at the link below. https://www.jstage.jst.go.jp/article/jwet/18/4/18_19-146/_supplement/_download/18_19-146_1.pdf

REFERENCES

[1] Gallen C, Drage D, Eaglesham G, Grant S, Bowman M, Mueller JF: Australia-wide assessment of perfluoroalkyl substances (PFASs) in landfill leachates. *J. Hazard. Mater.*, **331**(5), 132–141, 2017. PMID:28254660 doi:10.1016/j.jhazmat.2017.02.006

[2] Senthilkumar K, Ohi E, Sajwan K, Takasuga T, Kannan K: Perfluorinated compounds in river water, river sediment, market fish, and wildlife samples from Japan. *Bull. Environ. Contam. Toxicol.*, **79**(4), 427–431, 2007. PMID:17634852 doi:10.1007/s00128-007-9243-2

[3] Dalahmeh S, Tirgani S, Komakech AJ, Niwagaba CB, Ahrens L: Per- and polyfluoroalkyl substances (PFASs) in water, soil and plants in wetlands and agricultural areas in Kampala, Uganda. *Sci. Total Environ.*, **631–632**, 660–667, 2018. PMID:29539594 doi:10.1016/j.scitotenv.2018.03.024

[4] Joerss H, Apel C, Ebinghaus R: Emerging per- and polyfluoroalkyl substances (PFASs) in surface water and sediment of the North and Baltic Seas. *Sci. Total Environ.*, **686**, 360–369, 2019. PMID:31181522 doi:10.1016/j.scitotenv.2019.05.363

[5] Koch A, Kärrman A, Yeung LWY, Jonsson M, Ahrens L, Wang T: Point source characterization of per- and polyfluoroalkyl substances (PFASs) and extractable organofluorine (EOF) in freshwater and aquatic invertebrates. *Environ. Sci. Process. Impacts*, **21**(11), 1887–1898, 2019. PMID:31552402 doi:10.1039/C9EM00281B

[6] Yamashita N, Kannan K, Taniyasu S, Horii Y, Petrick G, Gamo T: A global survey of perfluorinated acids in oceans. *Mar. Pollut. Bull.*, **51**(8–12), 658–668, 2005. PMID:15913661 doi:10.1016/j.marpolbul.2005.04.026

[7] Kirchgeorg T, Dreyer A, Gabrielli P, Gabrieli J, Thompson LG, Barbante C, Ebinghaus R: Seasonal accumulation of persistent organic pollutants on a high altitude glacier in the Eastern Alps. *Environ. Pollut.*, **218**, 804–812, 2016. PMID:27554981 doi:10.1016/j.envpol.2016.08.004

[8] Houde M, Martin JW, Letcher RJ, Solomon KR, Muir DCG: Biological monitoring of polyfluoroalkyl substances: A review. *Environ. Sci. Technol.*, **40**(11), 3463–3473, 2006. PMID:16786681 doi:10.1021/es052580b

[9] Bodin J, Groeng EC, Andreassen M, Dirven H, Nygaard UC: Exposure to perfluoroundecanoic acid (PFUnDA) accelerates insulitis development in a mouse model of type 1 diabetes. *Toxicol. Rep.*, **3**, 664–672, 2016. PMID:28959590 doi:10.1016/j.toxrep.2016.08.009

[10] Boisvert G, Sonne C, Rigét FF, Dietz R, Letcher RJ: Bioaccumulation and biomagnification of perfluoroalkyl acids and precursors in East Greenland polar bears and their ringed seal prey. *Environ. Pollut.,* **252**(B), 1335–1343, 2019. PMID:31252132 doi:10.1016/j.envpol.2019.06.035

[11] Scheringer M, Trier X, Cousins IT, de Voogt P, Fletcher T, Wang Z, Webster TF: Helsingør Statement on poly- and perfluorinated alkyl substances (PFASs). *Chemosphere*, **114**, 337–339, 2014. PMID:24938172 doi:10.1016/j.chemosphere.2014.05.044

[12] Murakami M, Takizawa S: Current status and future prospects of pollution in water environments by perfluorinated surfactants. *J. Jpn. Soc. Water Environ.*, **33**(8), 103–114, 2010. [in Japanese with English abstract] doi:10.2965/jswe.33.103

[13] Takemine S, Matsumura C, Yamamoto K, Suzuki M, Tsurukawa M, Imaishi H, Nakano T, Kondo A: Discharge of perfluorinated compounds from rivers and their influence on the coastal seas of Hyogo prefecture, Japan. *Environ. Pollut.*, **184**, 397–404, 2014. PMID:24113473 doi:10.1016/j.envpol.2013.09.016

[14] Beškoski VP, Yamamoto K, Yamamoto A, Okamura H, Hayashi M, Nakano T, Matsumura C, Fukushi K, Wada S, Inui H: Distribution of perfluoroalkyl compounds in Osaka Bay and coastal waters of Western Japan. *Chemosphere*, **170**, 260–265, 2017. PMID:28006759 doi:10.1016/j.chemosphere.2016.12.028

[15] Beškoski VP, Takemine S, Nakano T, Slavković Beškoski L, Gojgić-Cvijović G, Ilić M, Miletić S, Vrvić MM: Perfluorinated compounds in sediment samples from the wastewater canal of Pančevo (Serbia) industrial area. *Chemosphere*, **91**(10), 1408–1415, 2013. PMID:23415492 doi:10.1016/j.chemosphere.2012.12.079

[16] MacInnis JJ, Lehnherr I, Muir DCG, Quinlan R, De Silva AO: Characterization of perfluoroalkyl substances in sediment cores from High and Low Arctic lakes in Canada. *Sci. Total Environ.*, **666**, 414–422, 2019. PMID:30802657 doi:10.1016/j.scitotenv.2019.02.210

[17] Zhao P, Xia X, Dong J, Xia N, Jiang X, Li Y, Zhu Y: Short- and long-chain perfluoroalkyl substances in the water, suspended particulate matter, and surface sediment of a turbid river. *Sci. Total Environ.*, **568**, 57–65, 2016. PMID:27285797 doi:10.1016/j.scitotenv.2016.05.221

[18] Lam NH, Cho CR, Kannan K, Cho HS: A nationwide survey of perfluorinated alkyl substances in waters, sediment and biota collected from aquatic environment in Vietnam: Distributions and bioconcentration profiles. *J. Hazard. Mater.*, **323**(Pt A), 116–127, 2017. PMID:27106518 doi:10.1016/j.jhazmat.2016.04.010

[19] Campo J, Lorenzo M, Pérez F, Picó Y, Farré M, Barceló D: Analysis of the presence of perfluoroalkyl substances in water, sediment and biota of the Jucar River (E Spain). Sources, partitioning and relationships with water physical characteristics. *Environ. Res.*, **147**, 503–512, 2016. PMID:26974364 doi:10.1016/j.envres.2016.03.010

[20] Kahkashan S, Wang X, Chen J, Bai Y, Ya M, Wu Y, Cai Y, Wang S, Saleem M, Aftab J, Inam A: Concentration, distribution and sources of perfluoroalkyl substances and organochlorine pesticides in surface sediments of the northern Bering Sea, Chukchi Sea and adjacent Arctic Ocean. *Chemosphere*, **235**, 959–968, 2019. PMID:31561312 doi:10.1016/j.chemosphere.2019.06.219

[21] Niisoe T, Senevirathna STMLD, Harada KH, Fujii Y, Hitomi T, Kobayashi H, Yan J, Zhao C, Oshima M, Koizumi A: Perfluorinated carboxylic acids discharged from the Yodo River Basin, Japan. *Chemosphere*, **138**, 81–88, 2015. PMID:26037820 doi:10.1016/j.chemosphere.2015.05.060

[22] Ahrens L, Taniyasu S, Yeung LWY, Yamashita N, Lam PKS, Ebinghaus R: Distribution of polyfluoroalkyl compounds in water, suspended particulate matter and sediment from Tokyo Bay, Japan. *Chemosphere*, **79**(3), 266–272, 2010. PMID:20181376 doi:10.1016/j.chemosphere.2010.01.045

[23] Ahrens L, Yamashita N, Yeung LWY, Taniyasu S, Horii Y, Lam PKS, Ebinghaus R: Partitioning behavior of per- and polyfluoroalkyl compounds between pore water and sediment in two sediment cores from Tokyo Bay, Japan. *Environ. Sci. Technol.*, **43**(18), 6969–6975, 2009. PMID:19806729 doi:10.1021/es901213s

[24] Latała A, Nędzi M, Stepnowski P: Acute toxicity assessment of perfluorinated carboxylic acids towards the Baltic microalgae. *Environ. Toxicol. Pharmacol.*, **28**(2), 167–171, 2009. PMID:21783999 doi:10.1016/j.etap.2009.03.010

[25] Asaoka S, Jadoon WA, Umehara A, Takeda K, Otani S, Ohono M, Fujitake N, Sakugawa H, Okamura H: Organic matter degradation characteristics of coastal marine sediments collected from the Seto Inland Sea, Japan. *Mar. Chem*. [in press] doi:10.1016/j.marchem.2020.103854

[26] Matsuda O, Koyama H, Matsushima H, Ogami T: Sedimentation rate and behavior of particulate phosphorus in eutrophic coastal environment. *J. Fac. Fish. Anim. Husb. Hiroshima Univ*., **16**, 45–58, 1977. doi:10.15027/41273

[27] Hoshika A: Sedimentation rates and heavy metal pollution of sediments in the Seto Inland Sea. In: Yanagi, T. (ed.), Bottom Environment of Seto Inland Sea, Kouseisha Kouseikaku Co., Ltd., Tokyo, Japan, pp. 17-32, 2008. [in Japanese]

[28] Hoshika A, Tanimoto T, Mishima Y: Sedimentation processes of particulate matter in the Osaka Bay. *Oceanography in Japan*, **3**(6), 419–425, 1994. [Japanese with English abstract] doi:10.5928/kaiyou.3.419

[29] Hoshika A, Shiozawa T, Matsumoto E: Sedimentation rate and heavy metal pollution in sediments in Harima Nada (Harima Sound), Seto Inland Sea. *J. Oceanogr. Soc. Jpn*., **39**(2), 82–87, 1983. [in Japanese with English Abstract] doi:10.1007/BF02210762